

Andrew D. J. Barnes, M. Grazia  
 Francesconi\* and Timothy J.  
 Prior

 Department of Chemistry, University of Hull,  
 Hull HU6 7RD, England

 Correspondence e-mail:  
 m.g.francesconi@hull.ac.uk

**Key indicators**

Single-crystal synchrotron study

 $T = 150 \text{ K}$ 

 Mean  $\sigma(a-O) = 0.014 \text{ \AA}$ 
 $R \text{ factor} = 0.035$ 
 $wR \text{ factor} = 0.088$ 

Data-to-parameter ratio = 17.5

 For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

## A synchrotron study of $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$

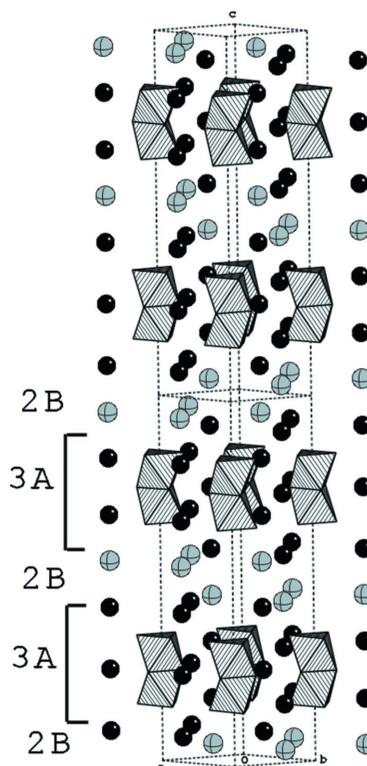
The structure of pentabarium ditantalum dichloride non-oxide,  $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$ , is isotypic with  $\text{Ba}_5\text{Ru}_{1.6}\text{W}_{0.4}\text{Cl}_2\text{O}_9$  and with one polymorph of  $\text{Ba}_5\text{Ru}_2\text{Cl}_2\text{O}_9$ . It is related to the perovskite structure and shows a ten-layer stacking of  $\text{BaO}_3$  and  $\text{BaCl}$  blocks along the  $c$  axis. The Ta cations occupy octahedral interstices, forming  $\text{Ta}_2\text{O}_9$  dimers of distorted face-shared  $\text{TaO}_6$  octahedra. Except for one O atom, all atoms are situated on special positions: Ba1 (Wyckoff position  $\bar{6}m2$ ), Ba2 and Ba3 ( $3m.$ ), Ta ( $3m.$ ), Cl ( $3m.$ ) and O1 ( $mm2$ ).

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**Comment**

Compounds showing perovskite-related structures are of great interest as they show a range of properties, such as ionic conductivity, superconductivity, colossal magnetoresistance and catalytic properties (Cava, 2001; Ishihara *et al.*, 1994; Rao & Raveau, 1998). Mixed-anion compounds are not as common as oxides showing perovskite-related structures, but these


**Figure 1**

The structure of  $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$ . The polyhedra represent the  $\text{Ta}_2\text{O}_9$  dimers of face-shared  $\text{TaO}_6$  octahedra. Grey and black spheres represent  $\text{Cl}^-$  and  $\text{Ba}^{2+}$ , respectively. The ten-layer stacking sequence,  $(BAAA)_2$ , with  $B = \text{BaCl}$  and  $A = \text{BaO}_3$ , is indicated.

offer a means of tuning physical properties by variation of the anion composition.

We have now prepared the chloride oxide  $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$ , which is isotypic with  $\text{Ba}_5\text{Ru}_{1.6}\text{W}_{0.4}\text{Cl}_2\text{O}_9$  (Hong & Sleight, 1997) and with one polymorph of  $\text{Ba}_5\text{Ru}_2\text{Cl}_2\text{O}_9$  (Tancret *et al.*, 2004).  $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$  is also structurally related to  $\text{Ba}_5\text{Ru-TaCl}_2\text{O}_9$  (Wilkens & Müller-Buschbaum, 1991), which was refined in the non-centrosymmetric space group  $P6_322$  due to differences in the O2 atomic coordinates. Although the reaction mixture contained  $\text{Ca}_3\text{N}_2$ , there was no evidence for the presence of Ca or N within the structure.

The structure of  $\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$  is shown in Fig. 1 and can be described as a ten-layer stacking of  $\text{BaO}_3$  and  $\text{BaCl}$  blocks along the  $c$  axis, in the sequence  $(BAAAB)_2$ , where  $A = \text{BaO}_3$  and  $B = \text{BaCl}$ . The Ta cations occupy the octahedral sites created by the three  $\text{BaO}_3$  layers, forming  $\text{Ta}_2\text{O}_9$  dimers of distorted face-shared  $\text{TaO}_6$  octahedra. Therefore, the structure can be described as an intergrowth of hexagonal perovskite blocks  $(\text{Ba}_3\text{Ta}_2\text{O}_9)^{2-}$  and of NaCl-type double layers  $(\text{Ba}_2\text{Cl}_2)^{2+}$ .

The six symmetry-equivalent terminal Ta–O bonds are 1.873 (13) Å in length, while the remaining six Ta–O bond lengths in the dimer are considerably longer, at 2.139 (11) Å. Ba1 is twelve-coordinated by six O2 [2.949 (12) Å] and six O1 [2.996 (11) Å]. Ba2 is ten-coordinated by three O1 [2.734 (11) Å], six O2 [2.949 (12) Å] and one Cl [3.113 (6) Å]. Ba3 is seven-coordinated by three O2 [2.562 (11) Å], one Cl [3.159 (7) Å] and three additional Cl atoms [3.557 (2) Å].

## Experimental

All operations had to be carried out under an inert atmosphere due to the extreme air- and moisture-sensitivity of the reagents. A mixture of polycrystalline  $\text{BaCl}_2$ ,  $\text{BaO}$  and  $\text{Ca}_3\text{N}_2$  (1:1:1 molar ratio) was placed in a crucible formed from tantalum metal foil and, subsequently, sealed inside a silica tube, with a valve head to allow the reaction to take place under flowing nitrogen. The mixture was heated for 36 h at 1273 K, then cooled to room temperature at 285 K h<sup>-1</sup>. A large number of yellow and orange crystals were found to have grown on the Ta foil. None of the orange crystals proved suitable for X-ray diffraction. A yellow block-like crystal was analysed at station 16.2SMX of the UK Synchrotron Radiation Source, Daresbury Laboratory.

### Crystal data

$\text{Ba}_5\text{Ta}_2\text{Cl}_2\text{O}_9$	$Z = 2$
$M_r = 1263.50$	Synchrotron radiation
Hexagonal, $P6_3/mmc$	$\lambda = 0.7848$ Å
$a = 5.9787$ (3) Å	$\mu = 27.18$ mm <sup>-1</sup>
$c = 24.796$ (3) Å	$T = 150$ (2) K
$V = 767.59$ (10) Å <sup>3</sup>	$0.04 \times 0.02 \times 0.02$ mm

### Data collection

Bruker APEXII CCD area-detector diffractometer	5409 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2004)	351 independent reflections
$T_{\min} = 0.337$ , $T_{\max} = 0.665$	317 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.093$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	20 parameters
$wR(F^2) = 0.088$	$\Delta\rho_{\text{max}} = 1.93$ e Å <sup>-3</sup>
$S = 1.12$	$\Delta\rho_{\text{min}} = -2.88$ e Å <sup>-3</sup>
351 reflections	

When refined with anisotropic displacement parameters, the O atoms gave physically unreasonable values. Therefore, the O atoms were refined with isotropic displacement parameters in the final model. The highest peak in the final difference Fourier map is located 0.67 Å from atom O2 and the deepest hole is located 1.46 Å from atom Ba1.

Data collection: *APEXII* (Bruker, 2004); cell refinement: *APEXII*; data reduction: *APEXII*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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